Synthesis and Properties of Polyquinolines and Polyanthrazolines Containing Pyrrole Units in the Main Chain

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ABSTRACT: A series of eight new polyquinolines and polyanthrazolines with pyrrole isomeric units in main chain were synthesized and characterized. The new polymers showed high glass transition temperatures ($T_g = 242-339$ °C) and excellent thermal stability ($T_{5\%} = 398-536$ °C in air, TGA). Compared to the series of polyanthrazolines, the series of polyquinolines exhibited higher thermal stability, better solubility in common organic solvents, and lower maximum absorption wavelengths (λ^a_{max}). Polyanthrazolines with 2,5-pyrrole linkage showed an unusually high λ^a_{max} (565 nm) and small band gap (2.02 eV). All polymers in solution had low photoluminescence quantum yields between 10^{-2}% and 10^{-5}% and excited-state lifetimes of 0.28−1.29 ns. The effects of molecular structure, especially pyrrole linkage structures, on the electronic structure, thermodynamics, and some of the optical properties of the polymers were explored. A model of hydrogen bonds in the main chain of the polymers was suggested to explain the difference in the properties of the isomer polymers. In addition, a polyquinoline (PBM) was chosen to examine the proton conductivity; the result indicated that the PBM/H_3PO_4 complex exhibited a high conductivity of 1.5×10^{-3} S cm^{-1} at 157 °C. The new polymers are expected to have improved proton-conducting properties for the application as the membranes in fuel cells.

Introduction

Polyquinolines were developed during the 1970s by Stille and co-workers in response to an increasing demand for polymeric materials with high thermal and oxidative stability.[1−3] Their synthetic chemistry, thermal properties, mechanical properties, and electrical and optical properties have been established by Stille,[4−7] Jenekhe,[8−11] Jen,[12−14] and their co-workers. Recently, optical and electronic properties of polyquinolines such as electroluminescent,[11] third-order nonlinear optical,[14] and optically active properties[15] have been studied extensively for their potential use in photonics and electronic applications. To date, a lot of polyquinolines with diverse structures have been synthesized and investigated.[16,17] Some polyquinolines with structural features exhibited special properties. Conjugated rigid-rod polyquinolines and polyanthrazolines have proven to be promising electronic and optoelectronic materials.[9,11] Thiophene-linked polyanthrazolines, which possessed low ionization potentials (∼4.8−4.9 eV) and high electron affinities (∼2.9 eV), showed significantly improved intrinsic electronic properties compared with those of the known phenylene-liked polyanthrazolines.[10a] By introducing silicon atom into the aromatic backbone[18] or through pendent side chains,[4] the solubility and processability of polyquinolines have been improved. Moreover, as a thermally stable support, polyquinolines containing the diphenylphosphine ligand have been used as catalysts in homogeneous catalytic reactions.[19] Chiral polyquinolines have been prepared in our laboratory.[15]

To our best knowledge, the proton conducting and optical properties of polyquinolines with active hydrogen have not been reported prior to this work. In this report, a new series of polyquinolines and polyanthrazolines containing pyrrole units with active hydrogen atoms were synthesized and characterized. The effects of molecular structure, especially pyrrole linkage structures, on the electronic structure, thermodynamics, and some of the optical properties of the polymers were explored. A model of hydrogen bonds in the main chain of the polymers was suggested to explain the difference in the properties of the isomer polymers. In addition, a polyquinoline (PBM) was chosen to examine the proton conductivity.

Experimental Section

General Procedures. Pyrrole and trifluoroacetic anhydride were purchased from Fluka. The PBI membrane (120 μm) was supplied by the Material Science Group of Technical University of Denmark. Pyrrole was purified by distillation. Tetrahydrofuran (THF) and benzene were distilled under nitrogen from sodium benzophenone ketyl. Other chemicals were obtained commercially and used as received unless otherwise specified.

Infrared spectra were recorded by using a Bio-Rad FTS-135 spectrophotometer. ^{1}H NMR spectra were obtained on a Varian Unity-400 (400 MHz) NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Elemental analyses were determined with an Elementar Analysensysteme GmbH VarioEL in CHN mode. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA-7 at a heating rate of 10 °C/min, and the differential scanning calorimetry (DSC) analyses were conducted with a Perkin-Elmer DSC-7 system at a heating rate of 10 °C/min under a nitrogen or air atmosphere. The dynamic mechanical property of PBM membrane was measured on a dynamic mechanical thermal analyzer (DMTA). Melting points were determined by using a XT-4 melting point apparatus and were uncorrected. Inherent viscosities of 0.5 g/dL polymer solutions in specified solvents were measured with an Ubbelodhe viscometer at 30 °C. Optical absorption spectroscopy was performed on Varian Cary 1E ultraviolet−visible spectrophotometer. Steady-state photolu-

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minescence studies were carried out by a Spex FL-2T2 spectrofluorimeter. The solutions of polymers for steady-state PL studies were positioned such that the light emission was detected at 90° from the incident beam. The PL quantum efficiencies (ϕ) of polymers were estimated by using a solution Rhodamine B (1×10^{-7} mol/L, in *m*-cresol containing 0.2 wt % di-*m*-cresyl phosphate (DCP)) as a standard ($\phi_{PL} = 95\%$) and referring to the method in the literature.[10c] Time-resolved photoluminescence decay measurements were performed using an Applied Photophysics SP-70 nanosecond spectrofluorimeter based on the time-correlated single photon counting technique. The excitation source was a N_2 lamp which had a ~3 ns pulse width at a repetition rate of 50 kHz. The samples were excited at 351 nm; the emission was collected at a 90° angle to the excitation beam. The PL decay was detected at the PL emission peak for each polymer. Alternating-current conductivities were measured between a pair of stainless steel electrodes at varying temperature using a Solortron 1255 impedance analyzer with the frequency range of 0.1 Hz−1 MHz and an oscillating voltage of 10 mV.

Optical quality thin films of the polymers were obtained by spin-coating onto silica substrates from their *m*-cresol (PAO, PAM, PBO, PBM) or *m*-cresol containing 0.2 wt % DCP solutions (PCO, PCM, PDO, PDM). The thin films were dried overnight at 125 °C in a vacuum or placed in ethanol containing 10 wt % triethylamine for 1−2 days and then dried overnight at 60 °C in a vacuum.

The proton conducting membrane was cast from a 6.6 wt % solution of polymer in DMAC containing 0.6 wt % LiCl as stabilizing agent by drawing on glass plates, using spacers to regulate its thickness. The cast solution was dried overnight at 60−70 °C and then dried at 130 °C under vacuum for 10 h. It was placed in boiling−water for 2−3 h to remove any traces of lithium and residual organic solvent, before being immersed in 6 mol/L H_3PO_4/water-ethanol (1:1.5) for 3−5 days. The membrane (200 μm) was washed with water and blotted with filter paper. The absorption level of H_3PO_4 in polymer/H_3PO_4 complex was determined by measuring the change in the mass before and after the immersion.

Monomer Synthesis. 4,4′-Bis(2-aminobenzoyl)diphenyl ether[2] (A), 4,6-dibenzoyl-1,3-phenylenediamine (C), and 2,5-dibenzoyl-1,4-phenylenediamine (D) were synthesized according to the literature.[1] 4,4′-Diamino-3,3′-dibenzoyldiphenyl ether (B) was prepared from *p*-chloronitrobenzene as a raw material by modifying a method reported.[15]

1-(*p*-Tolylsulfonyl)pyrrole, 1.[20] To a vigorously stirred solution of 43.6 mL (0.60 mol) of pyrrole and 400 mL of absolute tetrahydrofuran at 25 °C was slowly added 20 g (0.50 mol) of metal potassium. The mixture was allowed to heat to the reflux temperature and maintained at reflux until all of the metal had reacted (about 3 h). The white slurry was diluted with 350 mL of solvent, and a solution of 76.2 g (0.40 mol) of *p*-tolylsulfonly chloride (TsCl) in 450 mL of tetrahydrofuran was added dropwise over a period of 45 min. After the resulting mixture had been stirred at room temperature overnight, it was filtered to yield a solution which was evaporated to dryness under reduced pressure; the solid residue was treated with activated charcoal and recrystallized from methanol to give 53.9 g (61.0%) of white crystals, mp 105−106 °C (lit.[20] 104.5 °C).

1-(*p*-Tolysulfonyl)-2-acetylpyrrole, 2. To a solution of acetic anhydride (27 g, 0.26 mol) in 720 mL of 1,2-dichloroethane at 25 °C was added $BF_3 \cdot OEt_2$ (75 g, 0.52 mol). The mixture was stirred for 10 min, 1-(*p*-tolysulfonyl)pyrrole (50 g, 0.23 mol) in 240 mL of 1,2-dichloroethane was added, and the mixture was stirred at 25 °C for 2 h. The reaction was quenched with cold water, and the residue remaining after concentration at reduced pressure was recrystallized from chloroform−hexane (1:5) to afford 48.9 g of pure **2** (80.5%), mp 110−111 °C. ^{1}H NMR ($CDCl_3$): δ 7.85−7.98 (m, 2H), 7.40−7.65 (m, 2H), 7.85 (dd, 1H, H-5), 7.05 (dd, 1H, H-3), 6.35 (t, 1H, H-4), 2.35 (s, 3H, CH_3CO), and 2.44 (s, 3H, CH_3).

2-Acetylpyrrole, 3. To a stirred solution of 45 g (0.17 mol) of **2** in 300 mL of methanol was added dropwise 300 mL of 5 mol/L NaOH at room temperature. The solution was heated and refluxed for 4 h. After the methanol was evaporated at reduced pressure, the aqueous residue was extracted with ethyl acetate, and the extracts were washed with brine, dried over Na_2SO_4, and concentrated at reduced pressure to give 17.5 g (94.4%) of 2-acetylpyrrole, **3**, mp 89−90 °C (lit.[21] 89.5−90.5 °C). ^{1}H NMR ($CDCl_3$): δ 9.83 (br s, 1H, H-1), 7.05 (m, 1H, H-5), 6.93 (m, 1H, H-3), 6.25 (t, 1H, H-4), 2.42 (s, 3H, CH_3CO).

2,5-Diacetylpyrrole (O) and 2,4-Diacetylpyrrole (M).[21] To a stirred mixture of 14.2 g (0.234 mol) of glacial acetic acid and 37.8 g (0.390 mol) of trifluoroacetic anhydride under N_2 was added dropwise a solution of 17 g (0.156 mol) of **3** in 235 mL of dry benzene. The whole was stirred for 2 weeks at room temperature during which the color turned from cranberry to black. The mixture was poured into 160 mL of water containing 80 g (0.94 mol) of sodium bicarbonate, and the resulting solution (pH is about 7) was extracted with ethyl acetate (6 × 150 mL). Evaporation of the solvent from the dried (magnesium sulfate) extract left 24 g of black solid, which was triturated with 3 × 40 mL of hot water for 2 h. The triturate water was cooled and added 45 g of sodium chlorate and extracted with ethyl acetate (6 × 150 mL). Removal of the solvent from the dried extract gave 15.1 g of solid which was chromatographed in a column of silica gum (100−200 mesh). Elution with petroleum ether−diethyl ether (2:1) afforded three products. The first eluted product was the starting **3** (5.5 g, 32.4%), mp 89−90 °C. The second eluted product was 2,5-diacetylpyrrole O (3.81 g, 16.2%), mp 158−159 °C. Recrystallization from water−ethanol and dry nitromethane afford colorless needles, mp 160−160.5 °C (lit.[21] 159.5−160 °C). IR (KBr): 3309 (NH s), 3108 (CH sh), 1662, 1648 (CH_3CO), 1538, 1427, 1360, and 1252 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.91 (br s, 1H, H-1), 6.86 (d, 2H, H-3, H-4), and 2.49 (s, 6H, CH_3CO). Anal. Calcd for $C_8H_9NO_2$: C, 63.57; H, 6.00; N, 9.27. Found: C, 63.75; H, 5.94; N, 9.13. The third eluted product was 2,4-diacetylpyrrole M (10.6 g, 45.1%), mp 137−138 °C. Two recrystallizations from petroleum−THF, mp 139.5−140 °C (lit.[21] 139.5−140 °C). IR (KBr): 3178 (NH s), 2981 (CH w), 1662, 1643 (CH_3CO), 1556, 1497, 1440, 1381, 1284, 1217, 1156, 946, 935, and 843 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 10.17 (br s, 1H, H-1), 7.62 (two overlapping d, 1H, H-5), 7.32 (d, 1H, H-3), 2.48 (s,3H, CH_3CO), and 2.47 (s, 3H, CH_3CO). Anal. Calcd for $C_8H_9NO_2$: C, 63.57; H, 6.00; N, 9.27. Found: C, 63.59; H, 6.03; N, 8.99.

Polymer Synthesis. Poly(2,2′-(2,5-pyrryl)-4,4′-(*p*,*p*′-oxydiphenylene)bisquinoline), PAO. A solution of 6.64 g of di-*m*-cresyl phosphate (DCP)[7a] and 2.23 g of freshly distilled *m*-cresol was added to equimolar amounts (0.993 mmol) of both A (0.405 g) and O (0.150 g) in a cylindrical-shaped reaction flask fitted with a mechanical stirrer. The reactor was purged with argon for 5−10 min before the temperature was raised to 135−140 °C in about 30 min. As the viscosity of the reaction mixture increased with time, small amounts of *m*-cresol were added to the reaction mixture to facilitate efficient stirring. The reaction was maintained at this temperature for 60 h under static argon. After cooling, the resulting viscous solution was added dropwise into an agitated solution of 450 mL of ethanol containing 10% v/v of triethylamine. The precipitated polymer was then chopped in a blender and collected by suction filtration. The polymer was purified by continuous extraction in a Soxhlet extractor for 24 h with a ethanol solution contain 15% v/v triethylamine and dried at 100 °C under vacuum for 24 h to afford 0.444 g (92%) of pure polymer PAO.

IR (KBr): 3436 (ν(N−H)), 3060 (ν(C−H)), 1592 (ν(C−C)), 1543 (ν(C−N)), 1492 (ν(C−C)), 1424, 1393, 1348, 1231 (ν(C−O)), 1205, 1167, 1101, 1014, 835 (δ(C−H)), 761, 711, 595, 572 cm^{-1} (δ(C−H)). Anal. Calcd: C, 83.76; H, 4.34; N, 8.62. Found: C, 83.24; H, 4.18; N, 8.36.

Poly(2,2′-(2,4-pyrryl)-4,4′-(*p*,*p*′-oxydiphenylene)bisquinoline), PAM. Equimolar amounts (0.961 mmol each) of A and M were reacted in 6.41 g of DCP and 2.22 g of *m*-cresol with a procedure similar to that described above to give a yield of 91%.

IR (KBr): 3428(M(N−H)), 3058(M(C−H)), 1592 (ν(C−C)), 1544 (ν(C−N)), 1491 (ν(C−C)), 1415, 1394, 1349, 1232 (ν(C−O)), 1199, 1166, 1098, 1014, 946, 834 (δ(C−H)), 760, 699, 593, 574 cm^{-1} (δ(C−H)). Anal. Calcd: C, 83.76; H, 4.34; N, 8.62. Found: C, 82.84; H, 4.12; N, 8.01.

Poly(2,2′-(2,5-pyrryl))-6,6′-oxybis(4-phenylquinoline)), PBO. It was synthesized using a similar procedure as described in PAO with equimolar amounts (1.210 mmol each) of B and O as the monomers. 8.08 g of DCP with 2.69 g of *m*-cresol was used as the reaction medium; the polymerization reaction was allowed to proceed for 48 h at 140 °C, to give 0.572 g (97%) of pure PBO.

IR (KBr): 3441 (ν(N−H)), 3058 (ν(C−H)), 1610, 1590 (ν(C−C)), 1541 (ν(C−N)), 1488 (ν(C−C)), 1426, 1350, 1207 (ν(C−O)), 1116, 1067, 1030, 993, 923, 880, 830, 763 (δ(C−H)),699, (δ(C−H)), 622, 583 cm^{-1}. Anal. Calcd: C, 83.76; H, 4.34; N, 8.62. Found: C, 84.60; H, 4.35; N, 8.52.

Poly(2,2′-(2,4-pyrryl))-6,6′-oxybis(4-phenylquinoline)), PBM. Equimolar amounts (5.650 mmol each) of B and M were reacted in 37.1 g of DCP and 12.6 g of *m*-cresol and reacted with a procedure similar to that described in PAO, to give 2.700 g (98%) of pure PBM.

IR (KBr): 3429 (ν(N−H)), 3056 (ν(C−H)), 1610, 1590 (ν(C−C)), 1542 (ν(C−N)), 1486 (ν(C−C)), 1452, 1198 (ν(C−O)), 1113, 1067, 1029, 989, 924, 878, 826, 763 (δ(C−H)), 697 (δ(C−H)) 623, 584 cm^{-1}. Anal. Calcd: C, 83.76; H, 4.34; N, 8.62. Found: C, 82.92; H, 4.25; N, 8.34.

Poly(2,8-(2,5-pyrryl))-4,6-diphenyl-1,9-anthrazoline), PCO. The same procedure was used as for polyquinoline PAO, equimolar amounts (1.620 mmol each) of monomers C and O as starting materials, 10.8 g of DCP, and 3.60 g of *m*-cresol were used as the reaction medium; the polymerization reaction was allowed to proceed for 96 h at 140 °C to give 0.436 g (68%) of pure PCO.

IR (KBr): 3433 (ν(N−H)), 3052 (ν(C−H)), 1585, 1571 (ν(C−C)), 1536 (ν(C−N)), 1494 (ν(C−C)), 1452, 1349, 1231, 1211, 1107, 1048, 1029, 876, 754 (δ(C−H)), 700 (δ(C−H)), 619, 601 cm^{-1}. Anal. Calcd: C, 85.04; H, 4.33; N, 10.63. Found: C, 84.02; H, 4.05; N, 10.01.

Poly(2,8-(2,4-pyrryl))-4,6-diphenyl-1,9-anthrazoline), PCM. Equimolar amounts (1.270 mmol each) of C and M were mixed with 8.48 g of DCP and 2.83 g of *m*-cresol and reacted with a procedure similar to that described in PAO; the polymerization reaction was maintained at 140 °C for 72 h to afford 0.422 g (84%) of pure PCM.

IR (KBr): 3421 (ν(N−H)), 3052 (ν(C−H)), 1581, 1566 (ν(C−C)), 1520 (ν(C−N)),1492 (ν(C−C)), 1452, 1400, 1340, 1234, 1195, 1101, 1048, 1028, 993, 921, 877, 830, 755 (δ(C−H)), 697 (δ(C−H)), 619, 601 cm^{-1}. Anal. Calcd: C, 85.04; H, 4.33; N, 10.63. Found: C, 84.35; H, 4.25; N, 10.17.

Poly(2,7-(2,5-pyrryl))-4,9-diphenyl-1,6-anthrazoline), PDO. Equimolar amounts (1.550 mmol each) of D and O were mixed with 10.4 g of DCP and 3.45 g of *m*-cresol and reacted at 140 °C for 72 h to give 0.582 g (95%) of pure PDO.

IR (KBr): 3440 (ν(N−H)), 3055 (ν(C−H)), 1586, 1568 (ν(C−C)), 1529 (ν(C−N)), 1491 (ν(C−C)), 1338, 1192, 1029, 989, 931, 890, 759 (δ(C−H)), 696 (δ(C−H)), 614, 543 cm^{-1}. Anal. Calcd: C, 85.04; H, 4.33; N, 10.63. Found: C, 84.29; H, 4.35; N, 10.00.

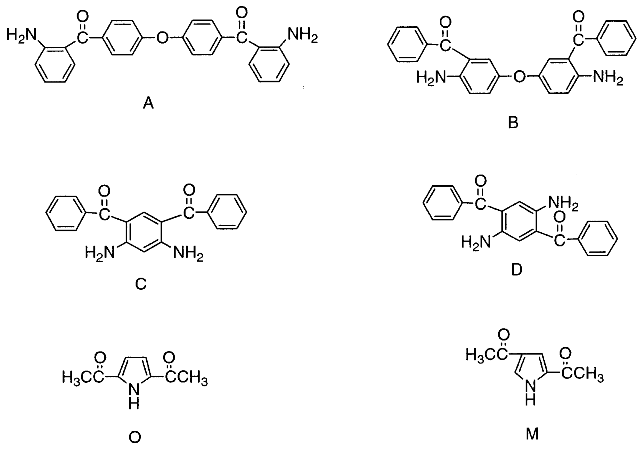
Poly(2,7-(2,4-pyrryl))-4,9-diphenyl-1,6-anthrazoline), PDM. Equimolar amounts (1.681 mmol each) of D and M were mixed with 11.2 g of DCP and 3.74 g of *m*-cresol and reacted at 140 °C for 72 h to afford 0.638 g (96%) of pure PDM.

IR (KBr): 3432 (ν(N−H)), 3052 (ν(C−H)), 1586,1570 (ν(C−C)), 1529 (ν(C−N)), 1490 (ν(C−C)), 1337, 1184, 1028, 985, 934, 885, 805, 760 (δ(C−H)), 696 (δ(C−H)), 616, 547 cm^{-1}. Anal. Calcd: C, 85.04; H, 4.33; N, 10.63. Found: C, 85.34; H, 4.68; N, 10.14.

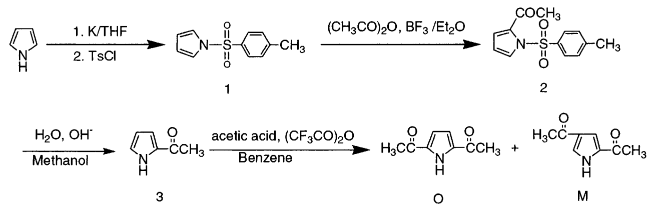
Results and Discussion

Monomers. Two diacetylaromatic monomers, 2,5-diacetylpyrrole (O) and 2,4-diacetylpyrrole (M), were synthesized from 2-acetylpyrrole (**3**). **3** was prepared by two different pathways. One synthetic method involved the direct acetylating of pyrrole with acetic anhydride under high temperature and high pressure to give a 38−40% yield of **3**.[22] But it was difficult to separate **3** from the reaction mixture from the stick gum. Another synthetic scheme that requires the protection of pyrrole hydrogen with *p*-tolylsulfonly is outlined in Scheme 2. The introduction of the protecting group was accomplished by the reaction of pyrrolylpotassium with *p*-tolylsulfonly chloride in tetrahydrofuran (THF). The reaction of 1-(*p*-tolylsulfonyl)pyrrole (**1**) with acetic anhydride by catalytic action of boron trifluoride ethyl ether complex afforded an 80.5% yield of 1-(*p*-tolylsulfonyl)-2-acetylpyrrole (**2**). The hydrolysis of **2** in methanol with 5 mol/L sodium hydroxide afforded a quantitative yield of **3**. The acetylation of **3** with acetic acid by trifluoroacetic anhydride as a catalyst gave O in 16.2% yield and M in 45.1% yield.

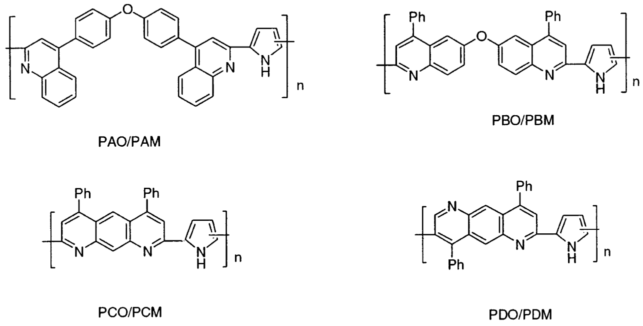
Scheme 1. Monomers



Scheme 2. Syntheses of Monomers O and M



Scheme 3. Polyquinolines and Polyanthrazolines



Polymers. The polymers containing quinoline and anthrazoline units were synthesized successfully using an equimolar mixture of the appropriate bis(*o*-aminoketone) (A, B, C, and D) and diacetyl monomers (O, M) with good yield. Their structures are sketched in Scheme 3 and denoted by P followed by the letters indicating the monomers used (hence, PAO, PAM, PBO, PBM, PCO, PCM, PDO, PDM). They comprised two groups (polyquinoline group and polyanthrazoline group), and each group was composed of four isomers. IR spectra of PBO and PBM are shown in Figure 1; the

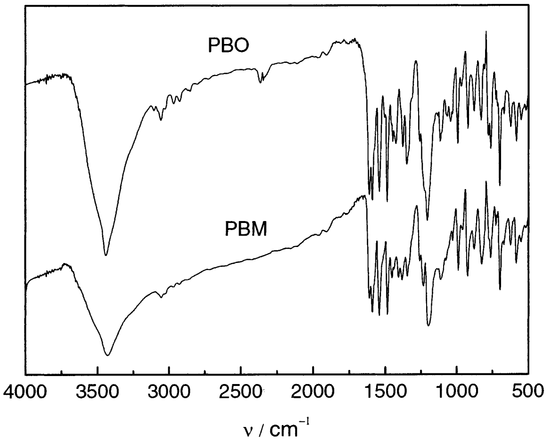


Figure 1. Infrared spectra of PBO and PBM.

Table 1. Properties of Polyquinolines and Polyanthrazolines

polymer	T_g[a] (°C)	$T_{5\%}$[b] (°C)	η_{inh} (dL/g)	solubility[e] CH$_3$Cl	DMAC	*m*-cresol	DCP/ *m*-cresol[f]
PAO	325	536	1.10[c]	I	PS	S	S
PAM	339	483	0.59[c]	PS	S	S	S
PBO	332	520	0.76[c]	PS	PS	S	S
PBM	319	455	1.41[c]	S	S	S	S
PCO	253	409	0.36[d]	I	I	PS	S
PCM	281	398	0.95[d]	I	I	PS	S
PDO	284	507	1.18[d]	I	I	PS	S
PDM	242	478	1.11[d]	I	I	PS	S

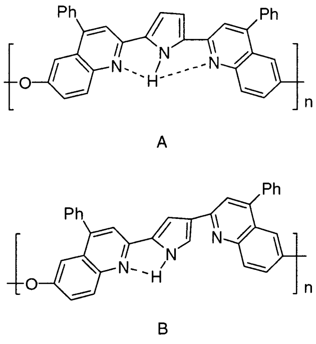
[a] DSC, second heating, 10 °C/min, nitrogen flow. [b] TGA, 5% weight loss in air at a heating rate of 10 °C/min. [c] Inherent viscosity measured with 0.5 g/dL in *m*-cresol at 30 °C. [d] Inherent viscosity measured with 0.5 g/dL in 2 wt % DCP/*m*-cresol at 30 °C. [e] S, soluble; I, insoluble; PS, partially soluble. [f] 2 wt % DCP in *m*-cresol.

absorption peak of N−H on pyrrole rings was found at 3441 and 3429 cm^{-1}, respectively.

Thermal Properties. Thermal properties of these polymers are summarized in Table 1. DSC measurement gave the glass transition temperatures (T_g) of the polymers in the range 242−339 °C, and TGA showed high thermal stability with the 5% weight loss ($T_{5\%}$) between 398 and 536 °C in air flow. Comparing the $T_{5\%}$'s of the polymers, it was found that PXO (the polymers based on 2,5-diacetylpyrrol, i.e., PAO, PBO, PCO, PDO) were more stable than the isomers PXM (PAM, PBM, PCM, PDM), and PDO and PDM have even higher thermal stability than PCO and PCM.

In the main chain of PXO, the pyrryl in two ortho positions to N−H was joined to ortho positions to N in the quinoline (or anthrazoline) rings (see Scheme 4), which was suggested to be beneficial to form more hydrogen bonds between quinoline N and pyrryl H than in the polymers based on 2,4-diacetylpyrrol PXM (one ortho and one meta position to N−H were joined in main chain) so that enhancing the main-chain bond strength. This effect was further verified by comparing the IR absorption peak of N−H of the polymers; i.e., the more hydrogen bonds formation also increased the bond strength of N−H, so the absorption wavenumbers (ν, cm^{-1}) in PXO were higher than that in PXM and PCO had the lowest molecular weight (see viscosity) in the series of polymers, which possibly was the main reason for the lower thermal stability than the other PXO.

Scheme 4. Conformations of the Hydrogen Bonds in PBO and PBM



Polyanthrazolines are the rigid-rod polymers; there is a large conjugated system along the main chain, retarding free rotation at the position of catenation and providing reduced chain mobility. In PCO and PCM the symmetry of anthrazoline unit is lower than that of the isoanthrazoline unit in PDO and PDM. Its two phenylene units are in the same side of the anthrazoline ring, and each anthrazoline unit puts a 120° kink in the main chain, so PCO and PCM are thought to be unfavorable for forming an ordered molecule and an extended chain conformation, especially in PCO containing 2,5-pyrryl with another about 120° kink in the main chain. The force forming more hydrogen bonds impelled anthrazoline unit and pyrryl to arrange in same orientation and developed coiled macromolecule, which possibly was a reason for PCO with the lowest molecular weight in the series of polymers, probably the crinkly structure may protected the formation of high molecular weight for PCO.

Solubility. As for most polyquinolines,[8,16a] all polymers described here are soluble in the protic or Lewis acid, for instance, sulfuric acid and the DCP/*m*-cresol solvent system. However, their solubility was different in common organic solvents. *m*-Cresol, *N*,*N*-dimethylacetamide (DMAC), and chloroform were chosen to test the solubility of the polymers; the results are summarized in Table 1.

From the solubility of Table 1, it was found an increasing sequence in solubility for the polymers: polyanthrazolines < PAO < PBO < PAM < PBM. As the rigid-rod polyquinolines reported,[4,5,8] polyanthrazolines without flexible linkage in backbone displayed insolubility in all tested solvents. PBM, with a flexible group in backbone, pendent phenyl side group,[18] and extended chain conformation, was the most soluble in the series of polymers. All polyquinolines could dissolve in *m*-cresol and were film-formable. With the exception of PCO, which has a low molecular weight, polyanthrazolines which only dissolved in DCP/*m*-cresol were also film-formable.

Optical Properties. The optical absorption spectra of thin films of the polymers are shown in Figures 2 and 3. Some optical properties of the polymers are compiled in Table 2. PDb[9b] and PDs[9b] were poly(1,6-anthrazoline)s with 1,4-phenylene linkage and 2,5-thiophene linkage, respectively, cited from literature for comparison. As can be seen from Figures 2 and 3 and Table 2, the maximum absorption wavelengths (λ^{a}_{max}) of thin films of polyquinolines and polyanthrazolines were located at 376−439 and 468−565 nm. Among them, λ^{a}_{max} of PDO(565 nm) and PDM (475 nm) were higher than that of PDb (443 nm). The fact indicated

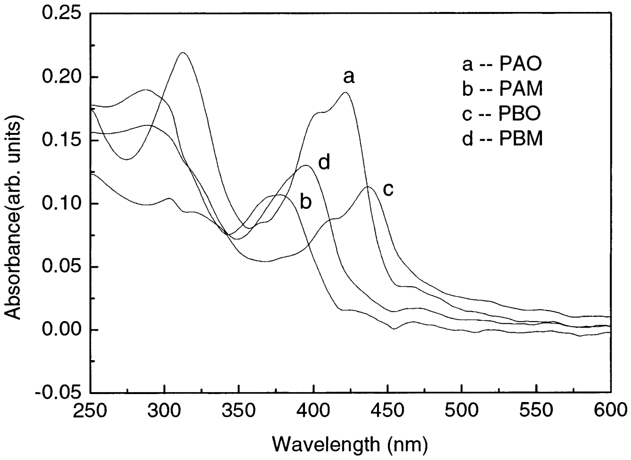


Figure 2. Optical absorption spectra of thin film of PAO, PAM, PBO, and PBM.

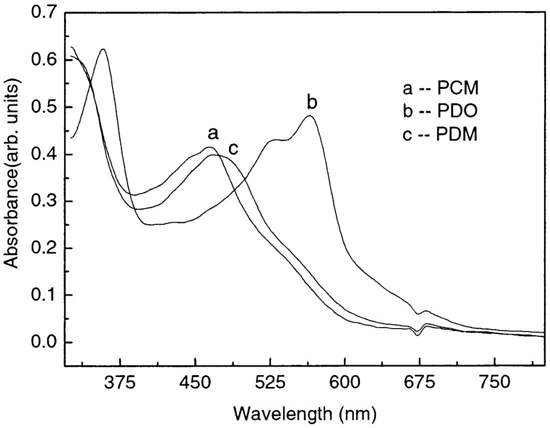


Figure 3. Optical absorption spectra of thin film of PCM, PDO, and PDM.

that the replacement of the phenylene linkage with the pyrrole linkage could produce the same effect as that with thiophene linkage,[9b] i.e., reducing the steric hindrance between the two adjacent aromatic rings in main chain, enhancing the conjugated electron delocalization and resulting in a significant red shift of λ^{a}_{max} of the polymers. In addition, PAO, PBO, and PDO have higher λ^{a}_{max} values by about 43−90 nm and smaller band gaps by ~0.1−0.3 eV than the corresponding isomers PAM, PBM, and PDM. These results illustrated that, compared with the polymers containing a 2,4-pyrryl unit, the polymers containing a 2,5-pyrryl unit PXO possessing more hydrogen bonds between quinoline N and pyrrole H were favorable for forming coplane of aromatic rings to enhance the conjugated electron delocalization. That also was proved by a red shift of about 67 nm in λ^{a}_{max} of PDO compared with PDs. Polyanthrazolines exhibited higher λ^{a}_{max} values by about 20−190 nm and smaller bands gaps by about 0.2−1.0 eV than polyquinolines, which could be attributed to a large extent of π-electron delocalization in the full conjugated molecule of polyanthrazolines with three fused rings.

The solution optical absorption spectra of the eight polymers in 0.2 wt % DCP/*m*-cresol are shown in Figures 4 and 5. Since some effects of intermolecular interactions on the polymer chain conformations could be negligible in solution, the effect of the pyrryl structures was expected to be more evident in the solution spectra than in thin-film spectra. Table 2 lists the values for λ^{a}_{max} in the solution spectra for all the polymers. As can be seen from Figures 5 and 6 and Table 2 that the order of increasing λ^{a}_{max} and, hence, the order of increasing π-electron delocalization is PAM < PBM < PAO < PBO < PCM < PDM < PDO < PCO, which is in the same order as that observed in the solid-state spectra.

Compared with the solid-state spectra of all the polymers, their respective solution spectra showed a great red shift by about 42−46 nm for polyquinolines with O structure, 50−53 nm for that with M structure, and 87−92 nm for polyanthrazolines. This strong bathochromic shift may be the consequence of the complexation reaction between the weakly acid DCP molecule and the basic nitrogen atoms of the polymers; the effect is similar to that seen in other polyquinolines[8,9b] and arises from the more extended-chain molecule and the more planar conformation of the protonated polymers. Because of the low photoluminescence (PL) efficiencies (ϕ), 10^{-2}%−10^{-5}% in solution, it is difficult to examine the PL spectra in solid. Figures 6 and 7 are the PL spectra of the polymers in solution (0.2 wt % DCP/*m*-cresol) which were excited at 342, 350, 350, 400, 350, 468, 468, and 468 nm for PAM, PBM, PAO, PBO, PCM, PDM, PDO, and PCO, respectively. The PL emission peaks (λ^{e}_{max}) are shown in Table 2. They have a same order as that observed in optical absorption spectra. The solution PL spectra showed that the emission colors of the polymers could be turned from green (PAM, PBM) to yellow (PAO PBO), orange (PCM, PDM), and red (PDO, PCO). By comparing the optical absorption and PL spectra of the polymers in solution, it could be seen that polymers have Stokes shifts of 45−75 nm, which is characteristic of excimer emission of many conjugated polymers.[10c]

To have a better understanding of the underlying photophysical process on molecules of the polymers in solution, the PL decay dynamics of the polymers were observed. It was found that the PL decay dynamics of all the polymers could best be described by two term exponential functions with one dominant lifetime. The best fit two lifetimes (τ_1 and τ_1) and their amplitudes for each polymer are given in Table 2. The multiple lifetimes needed to describe the PL decay dynamics of the polymers suggested the existence of more than one excited-state species or the occurrence of various excited-state progresses. The dominant PL lifetimes (τ_1) of PAO, PAM, and PDM were 1.29, 1.18, and 1.21 ns. These were in accordance with those of full conjugated polyquinolines (1.80−5.22 ns) in the solid state, but the dominant PL lifetimes of PBO, PBM, PCO, PCM, and PDO were in the range of 0.28 ns for PDO to 0.69 ns for PBM, which were identical with those of other luminescent conjugated polymers which typically have dominant lifetimes on the order of 100−600 ps.[10c]

The second PL lifetimes (τ_2) of all polymers, expect for PCM and PDM, are in the range of 6.30−8.30 ns. PCM and PDM possessed long second PL lifetimes, 18.5 and 16.1 ns, respectively. The lifetimes of the polymers were different from those of other polylquinolines in the solid state.[10c] That was thought to be due to their polarty in molecular repeating units changed by the protonation of the polymers in solution.

The PL quantum efficiencies (ϕ) estimated of the polymers in solution are shown in Table 2. They were very low in the range of 10^{-4} for PBM to 10^{-7} for PDO and PDM. This fact could be attributed to the existence of active hydrogen of pyrryls in polymers. From the PL quantum efficiencies and measured dominant PL life-

Table 2. Photophysical Properties of Polyquinolines and Polyanthrazolines[a]

polymer	λ^{a}_{max}(film), nm	E_g(film), eV	λ^{a}_{max}(soln), nm	λ^{e}_{max}(soln), nm	log (ϵ)[c]	ϕ_{PL}, %	τ_1, ns	τ_2, ns	amplitude, % τ_1/τ_2
PAO	422	2.79	468	532	4.99	2×10^{-3}	1.29	7.60	90.5/9.5
PAM	376	2.98	426	500	4.85	2×10^{-3}	1.18	7.39	97.1/2.9
PBO	439	2.67	497	561	4.69	2×10^{-3}	0.40	8.30	98.8/1.2
PBM	396	2.92	449	507	4.78	2×10^{-2}	0.69	7.58	97.0/3.0
PCO			660	725	4.89	4×10^{-4}	0.56	6.30	98.8/1.2
PCM	468	2.09	560	607	4.89	2×10^{-4}	0.68	18.5	97.1/2.9
PDO	565	2.02	653	709	4.88	2×10^{-5}	0.28	7.60	99.3/0.7
PDM	475	2.13	562	608	4.95	6×10^{-5}	1.21	16.1	97.4/2.6
PDb[b]	443	2.47	442		4.49				
PDs[b]	498	2.17	572		4.49				

[a] All solution spectra examined in 0.2 wt % DCP/*m*-cresol. [b] The data from the literature.[9b] [c] ϵ = molar absorption coefficient.

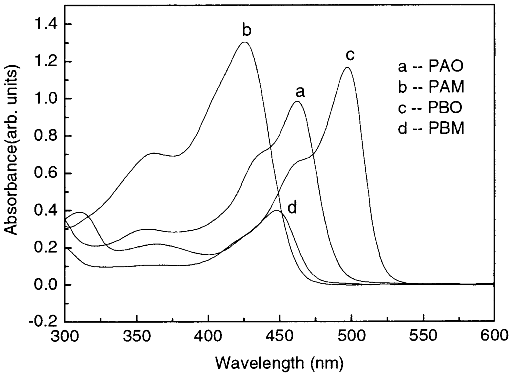


Figure 4. Optical absorption spectra of PAO, PAM, PBO, and PBM in solution (0.2 wt % DCP/*m*-cresol).

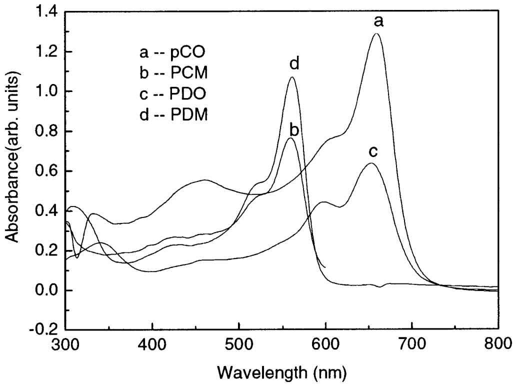


Figure 5. Optical absorption spectra of PCO, PCM, PDO, and PDM in solution (0.2 wt % DCP/*m*-cresol).

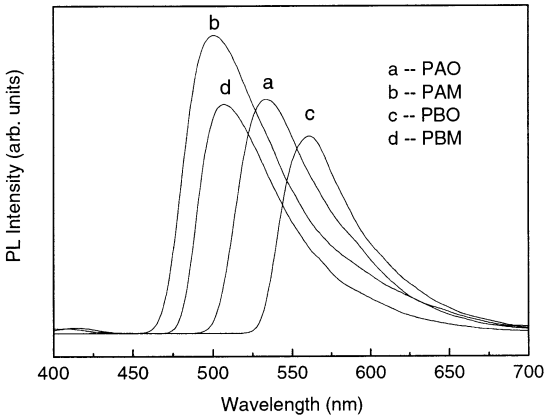


Figure 6. PL spectra of PAO, PAM, PBO, and PBM in solution (0.2 wt % DCP/*m*-cresol).

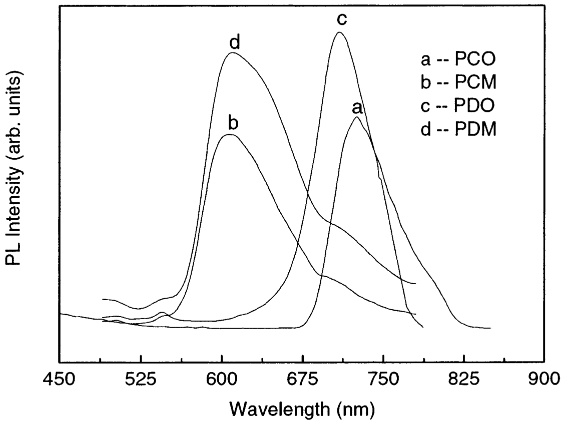


Figure 7. PL spectra of PCO, PCM, PDO, and PDM in solution (0.2 wt % DCP/*m*-cresol).

times of the polymers, the excited-state decay rate constants, the radiative rate constant k_r, and nonradiative rate constant k_{nr} could be estimated. For example, PBM with 2×10^{-4} PL quantum efficiency and dominant lifetime of 0.69 ns has a $k_r \sim 3 \times 10^5$ s^{-1} and $k_{nr} \sim 1 \times 10^9$ s^{-1}; the k_r of other polylquinolines was on the order of 10^4 s^{-1} and the k_{nr} was on the order of 10^8–10^9 s^{-1}, but PCO, PCM and PDO, PDM were on the order of 10^3 s^{-1}, 10^4 s^{-1} in k_r and 10^9 s^{-1}, 10^8–10^9 s^{-1} in k_{nr}, respectively. These estimates showed that the polymers forming ground-state aggregates had reduced emission and enhanced nonradiative decay rates compared to those forming excimers and the isomeric polymers have different ways of energy transition in the luminophor of polymers.

Conductivity. PBM with good solubility in DMAC was chosen to examine the proton conductivity. For comparison, the PBI was also measured in same experimental conditions. Temperature dependences of conductivity for PBM/H_3PO_4 and PBI/H_3PO_4 complexes at 3.8 and 1.5 mol unit^{-1}, respectively, are shown in Figure 8. As can be seen from Figure 8, the conductivities of PBM/H_3PO_4 and PBI/H_3PO_4 complexes increased with temperature, and the PBM/H_3PO_4 complex exhibited a higher conductivity compared with that of the PBI/H_3PO_4 complex, reaching 1.5×10^{-3} S cm^{-1} at 157 °C, while the conductivity of PBI/H_3PO_4 complex was 7×10^{-5} S cm^{-1} at 150 °C, which was in accordance with the result reported.[23] In addition, in same experimental conditions, PBM could complex more H_3PO_4 (3.8 mol unit^{-1}) than PBI (1.5 mol unit^{-1}). That may be the main reason for PBM/H_3PO_4 to have a higher conductivity.

Dynamic Mechanical Behavior. Figure 9 displays the dynamic storage modulus (E') and loss modulus (E'') as a function of temperature for PBM membrane without acid doping. Regarding the peak temperature in the E'' curve as the T_g, PBM exhibited T_g at 305 °C,

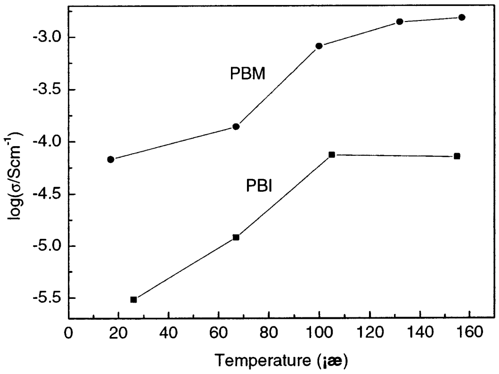


Figure 8. Temperature dependence of conductivity for PBM/H_3PO_4 and PBI/H_3PO_4 complexes at 3.8 and 1.5 mol unit^{-1}, respectively.

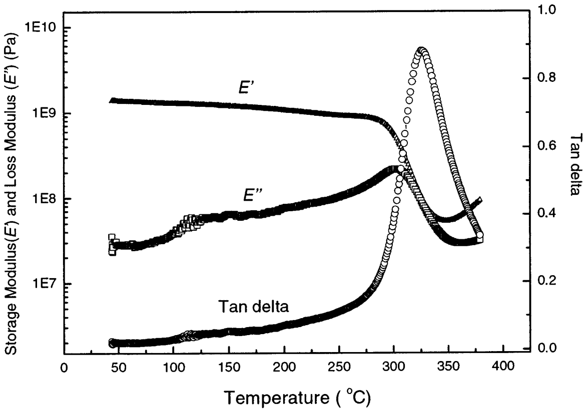


Figure 9. Dynamic modulus as a function of temperature for PBM membrane without acid doping (200 μm).

which agrees with T_g by DSC. PBM also showed a high modulus preservation before 290 °C.

Conclusions

A series of eight new polyquinolines and polyanthrazolines with pyrrole isomeric units in the main chain were synthesized and characterized. The new polymers showed high thermal stability, and some of them are soluble in common organic solvents. Some thermal and optical properties of polyquinolines mainly depended on the structure of pyrrole linkage, while that of polyanthrazolines were influenced by the structure of anthrazoline and pyrrole linkage. The pyrrole N−H with quinoline N was thought to form hydrogen bonds and enhance the main-chain bond strength, so that improving thermal stability, π-electron delocalization of the polymer backbone. This effect was further verified by comparing the IR absorption peak of N−H of the polymers. The result of conductivity measured of PBM showed that some of the polymers have great potentiality for the applications as proton conducting materials.

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